

[DESCRIPTION]**FIELD OF THE INVENTION**

The present invention relates to the manufacturing of a Thin Film Inorganic Light Emitting Diode.

BACKGROUND OF THE INVENTION

At present several thin film electroluminescent devices (ELDs) exist or are still in development. They are all characterized by one (or more) electroluminescent active layer(s) sandwiched between two electrodes. Optionally a dielectric layer may also occur. The substrate can be plastic or glass.

The thin film ELDs can be subdivided into the organic and the inorganic based ELDs. The organic based thin film ELDs⁽¹⁾ are further subdivided into Organic molecular or Oligomeric Light Emitting Diodes (OLEDs) and Polymer Light Emitting Diodes (PLEDs). The inorganic ELDs on the other hand can be further subdivided into the High Voltage Alternating Current (HV-AC) ELDs and the Low Voltage Direct Current (LV-DC) ELDs. Amongst the HV-AC ELDs, one can distinguish Thin Film ElectroLuminescent Devices (TFEL devices or TFELDs) and Powder ELDs (PEL Devices or PELDs). Amongst LV-DC ELDs one can distinguish Powder ELDs (DC-PEL Devices or DC-PELDs) and thin film DC-ELDs, hereinafter called Inorganic Light Emitting Diodes (ILEDs).

The basic construction of organic ELDs (PLED and OLED) comprises following layer arrangement : a transparent substrate (glass or flexible plastic), a transparent conductor, e.g. Indium Tin Oxide (ITO), a hole transporting layer, a luminescent layer, and a second electrode, e.g. a Ca, Mg/Ag or Al/Li electrode. For OLEDs the hole transporting layer and the luminescent layer are 10-50 nm thick and applied by vacuum deposition ; for PLEDs the hole transporting layer is 40 nm thick and the luminescent layer is 100

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nm and applied by spin coating. Between both electrodes a direct voltage of 5 - 10 V is applied.

For OLEDs the hole transporting layer and electroluminescent layer consist of low molecular organic compounds, including oligomers. E.g. N,N'-diphenyl-1,1'-biphenyl-4,4'-diamine (TPD) can be used as hole transporter, and as electroluminescent compounds the aluminium (III) 8-hydroxyquinoline complex (Alq_3), polyaromatics (anthracene derivatives, perylene derivatives and stilbene derivatives) and polyhetero-aromatics (oxazoles, oxadiazoles, thiazoles etc.) can be used. The main advantages of these low molecular OLEDs include high fluorescent quantum yield, high purification and crystal growth capability and a wide selection of material design. Crystallisation of initially amorphous samples, production of exciplexes with other materials, and often high chemical reactivity create serious problems in their application to stable EL systems. Moreover, the layers are applied by using vacuum-vapour deposition techniques, which are often cumbersome and expensive. However, recently monochromic displays based on this principle are launched on the market by Pioneer⁽³⁾.

On the other hand the electroluminescent compounds that can be used in PLEDs are polymers like the non-conjugated polyvinylcarbazole derivatives (PVK) or the conjugated polymers like poly(p-phenylene vinylenes) (PPV), poly(3-alkylthiophene, poly(p-phenylene ethynylens) etc. These high molecular weight materials allow for the easy preparation of thin films by casting, and show a high resistance to crystallization. The difficulties in purification procedures (and hence reproducability) and, mostly, a low fluorescent quantum yield, in addition to a complex structure and high sensitivity towards oxygen and moisture are severe drawbacks in their application to organic ELDs.

As mentioned before, today, two kinds of HV-AC inorganic based ELDs exist ⁽²⁾: PELDs and TFELDs. PEL Devices are used mainly for backlighting and low information content displays and can be manufactured on flexible substrates. TFEL devices are used for high information content matrix displays and can only be produced on glass substrates, due to the high processing temperature needed.

Their basic structure is essentially the same. A PELD consists of a transparent substrate, a transparent conductor (ITO), a luminescent layer of doped ZnS (50 μm), an insulator/reflector layer (50 μm), and a top electrode, e.g. Ag-paste. Between both electrodes an alternating voltage of 110 V and 400 Hz is applied. A TFEL device consists of a transparent substrate, a transparent conductor, and a luminescent phosphor layer (0.6 μm) between two moisture protective insulator layers (0.6 μm), and a top electrode, e.g. evaporated metal. Between both electrodes an alternating voltage of 200 V and 400 Hz is applied.

For both devices, doped ZnS is used as the active luminescent layer. The doping centers (e.g., Mn^{2+} , Cu^+) can be excited by the impact of injected electrons by means of a high electric field or by transfer of recombination energy towards an electroluminescent centre. These excited centers relax to the ground state by a luminescence process. Several mechanisms for the electroluminescence process have been proposed⁽⁴⁾. The insulating layer for the PELD (screen printed $BaTiO_3$ -powder + binder) fulfils three functions: (1) it prevents catastrophic breakdowns, (2) due to the high dielectric constant, the electric field will predominantly be focussed over the ZnS layer and (3) it will serve as diffuse light reflector, which increases the light output. For the TFEL device the vacuum deposited Al_2O_3 prevents also catastrophic breakdowns and it functions as tunnelling barrier for the electron injection. The structures are completed by two electrodes, one of which should be transparent.

For the PEL device, the ZnS layer comprises ZnS powder doped with copper ions and possibly other elements like chlorine and manganese mixed in an organic binder with a high dielectric constant like polyvinylidene fluoride or some kind of cyanoresin. The powders are prepared by high temperature sintering processes (> 700 °C) in order to allow diffusion of the dopants into the ZnS crystal matrix and integration of Cu_xS -rich needles in- and outside the ZnS lattice after cooling. For the HV-AC PELDs, the Cu_xS -needles at the surface are chemically removed by etching with cyanide ions. This to ensure electrical isolating particles. After that the particles are provided with a moisture protective layer like Al_2O_3 or NC (carbon-

nitride) in order to increase the lifetime of the phosphor. The particle size of these powders varies between 2 - 20 μm . The dispersion of this powders can be used in a screen printing process in order to apply them in an electroluminescent layer with a thickness of 50 - 100 μm .

Upon applying an electric field on the phosphor particles, charges (e.g. electrons) are generated inside the particles at stacking faults in the ZnS lattice and/or in the Cu_xS needles. These charges can move according to the direction of the applied field (AC). By this way recombination processes can occur whereby the recombination energy can be transferred to an electroluminescent centre (e.g. Cu^+ or Mn^{2+}). Also direct impact excitation of the luminescence centre can occur if the kinetic energy of the electron is high enough (ca 4 - 5 eV). These processes can give rise to electroluminescence.

Electroluminescence occurs normally at field strengths in the order of 1-2 MV/cm. For a layer thickness of 100 μm , applying 110 V results in a mean value of the field strength of 50 kV/cm. The Cu_xS needles at the interior of the ZnS-particles increase locally the electric field strength by a factor of 50 to 100 resulting in field strength values of up to 1 MV/cm, thereby making electroluminescence possible. The thick layer causes a slow luminance-voltage response, making PEL devices unsuitable for display applications.

General drawbacks of these PELDs are price (large amounts of products needed (about 150 g phosphor per square meter), the expensive BaTiO_3 layer, the high driving voltages (around 110 V) and their inherent instability. The latter is caused by the slowly decrease in number of crystal stacking faults and Cu_xS needles by applying an electric field (recrystallisation). The less stacking faults or Cu_xS needles, the less charges (electrons) can be generated and hence a decrease in light output can be expected.

For the TFEL device, the doped ZnS layer is preferably deposited by using the Atomic Layer Epitaxy technology (Planar International), which also requires a high temperature sintering step, thereby limiting the substrates to glass substrates. The formed doped ZnS-layer is crystalline. This layer is sandwiched

between two thin isolating Al_2O_3 layers. Upon applying a high voltage, typically between 150 – 200 V, tunneling of electrons occurs through these Al_2O_3 layers. Due to the high crystallinity of the ZnS layer, the electrons can travel freely under the influence of the applied electric field in this doped ZnS layer, thereby accumulating kinetic energy. At accumulation values of about 4 – 5 eV, impact excitation of the dopant can occur resulting in electroluminescence. The thin electroluminescent layer (1 – 1.5 μm) shows a threshold behaviour of the luminance-voltage curve, making this TFEL device suitable for display applications.

General drawbacks of this system are the slow and expensive production process and the necessity of complete protection against ambient humidity.

Low voltage DC PEL Devices were developed by Vecht et al as described by Chadha⁽⁵⁾. They used the same phosphor particles as for the AC-PELDs, but the conductive Cu_xS-needles at the surface are not removed. The general construction consists of a transparent substrate, a transparent conductor (ITO), a doped ZnS phosphor layer (20µm), and a top electrode (evaporated Alu).

The phosphor layer is applied by means of the doctor blade technique or screen printing on an ITO conducting layer. Subsequently an Alu electrode is evaporated. Upon applying a direct current voltage of several volts (ITO positive), the p-conductive Cu_xS starts moving towards the Alu electrode, thereby creating an insulating region (about 1 μm in thickness) next to the ITO layer within one minute or so. This results in a current drop which is associated with the onset of light emission. This process has been called the forming process. In this formed thin high resistive phosphor layer, high electric fields occur and electroluminescence is already possible at low voltages (typically between 10 and 30 V).

Major drawbacks of this system are the irreproducability of the forming process and the necessity of complete encapsulation against moisture. Also the preparation of the phosphor particles requires high sintering temperatures. No commercial devices based on this principle are on the market today.

Recently, several research groups reported photo-⁽⁷⁻¹³⁾ and electroluminescence⁽¹⁴⁻¹⁸⁾ from inorganic semiconducting nano particles.

Colvin et al.⁽¹⁴⁾ reported on the electroluminescence of CdSe nano-particles stabilized by hexane dithiol. They demonstrated EL for two devices comprising a spincoated double layer of CdSe and PPV on ITO and covered it with an evaporated Mg electrode. Depending on the voltage they observed emission from the CdSe (lower voltages) or from the PPV (higher voltages).

Electroluminescence of CdSe quantum-dot/polymer composites was also reported by Dabbousi et al.⁽¹⁵⁾. They spincoated on ITO one single layer of CdSe nano-particles stabilized with trioctylphosphine oxide and mixed with a polymeric hole transporter (PVK) and an electron transport species (an oxadiazole derivative of PVK, t-Bu-PBD). An aluminum electrode was subsequently evaporated. The system showed electroluminescence in reverse bias, and depending on the applied voltage the emission spectrum of the CdSe quantumdots or PVK was observed.

Gao et al.⁽¹⁶⁾ reported on the electroluminescence of self-assembled films of PPV and CdSe nano-particles. They could observe electroluminescence from the CdSe particles and/or from the PPV, depending on the applied voltage.

These examples demonstrate the possible use of inorganic nano-particles with semiconductor properties as Light Emitting Diodes (ILED), in analogy with the OLEDs. However, the use of Cd- or Se-compounds can not be recommended due to environmental problems that can be expected.

Huang et al.⁽¹⁷⁾ reported the photo- and electroluminescence of a single layer of ZnS:Cu nanocrystals spincoated on a ITO substrate and evaporated with an aluminum electrode. ZnS and Cu_xS are much more environmental friendly compared to CdSe. Also there was no need for organic hole or electron transporters, which can cause stability problems as is known in the organic PELDs. The drawback of their system lies in the fact that the synthesis of the ZnS:Cu particles is quite cumbersome and results in low yields. Polystyrene sulphonic acid is used as polyelectrolyte on which Zn and Cu ions are attached. Subsequently this polyelectrolyte is solved in

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dimethylformamide and reacted with H₂S. By this way ZnS:C_xS particles are formed.

Que et al.⁽¹⁸⁾ reported photo- and electroluminescence from a copper doped ZnS nanocrystals/polymer composite. The synthesis of the nano-particles was carried out by using the inverse microemulsion method. After washing and drying the ZnS:Cu powder was redispersed in MEK with PMMA as a binder and spincoated on ITO and evaporated with an aluminum electrode. Green electroluminescence could be observed in both bias directions at 5 V. The drawback of the fabrication of this device is the low concentrations of the ZnS:Cu dispersion that can be obtained (ca 10⁻³ M). Further it needs a well defined two phase system (soap/water). Also a drawback could be the solvent based spincoating dispersion.

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OBJECTS OF THE INVENTION

It is an object of the present invention to provide an easy and economical method for the manufacturing of a Thin Film Inorganic Light Emitting Diode device.

SUMMARY OF THE INVENTION

The above mentioned objects are realised by providing a method for the preparation of a Thin Film Inorganic Light Emitting Diode device, said method comprising the following steps, in order, :

- (1) preparing a nanoparticle dispersion of ZnS doped with a luminescent centre by precipitation from appropriate aqueous solutions comprising zinc ions, sulfide ions and dopant ions,

- (2) washing said dispersion of doped ZnS to remove non-precipitated ions,
- (3) coating onto a first conductive electrode said washed dispersion of doped ZnS, optionally after admixture with a binder,
- (4) applying on top of said coated layer resulting from step (3) a second conductive electrode, with the proviso that at least one of said first and second electrode is transparent.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig 1 illustrates the construction of an ILED device according to example 1.4 (see furtheron). Fig. 1a represents the layer arrangement before patterning. It comprises a PET substrate 20, a first conductive ITO layer 21, a luminescent layer 22 based on doped ZnS, and a second electrode layer of evaporated aluminum 23. Figures 1b, 1c and 1d separately represent the patterning of layers 21, 22, and 23 respectively. Fig. 1e represents a top view of the complete patterned ILED. 31 represents a direct current-voltage source (I/V source) connected to the ITO electrode and the aluminum electrode via contact points 32 and 33.

Fig 2 illustrates the construction of an ILED device according to example 1.5. In this case the ITO electrode is replaced by an ORGACON (trade mark of Agfa-Gevaert N.V.) foil.

DETAILED DESCRIPTION OF THE INVENTION

The present invention will now be explained in detail on the hand of its preferred embodiments.

In a preferred embodiment the precipitation of the doped ZnS particles is performed according to the double jet principle. In this technique a first and a second aqueous solution are added simultaneously to a third solution under controlled circumstances of temperature and flow rate. In this case the first solution contains the zinc ions and the second solution contains the sulfide ions. A useful zinc salt is zinc acetate. A useful sulfide is sodium sulfide. The dopant ions providing a luminescent centre can be present in the third solution, but more preferably, they are also

incorporated in the first solution containing the zinc salt. The Zns can be doped with ions of e.g. Cu, Mn, Ag, Tb, Eu, etc.. The most preferred dopants, however, are monovalent and divalent copper ions, and divalent manganese ions. Preferred copper salts are the acetate and the chloride. A preferred manganese salt is manganese acetate.

When the dopant is copper a complexing agent such a Na-EDTA or citrate may be incorporated in a solution involved in the precipitation, preferably the solution containing the copper ions. It is believed that this enhances the efficiency of the building in of copper in the ZnS lattice. Furtheron one of the solutions, preferably the third solution, may contain a diazole or triazole compound, e.g. 5-methyl-1,2,4-triazolo-(1,5-a)-pyrimidine-7-ol.

The resulting nanoparticle dispersion, or predispersion as it will be called in the examples, has to be washed and concentrated. This is preferably done by a diafiltration treatment. The diafiltration is preferably performed in the presence of a compound capable of preventing agglomeration of nanoparticles. The nature of this compound is not restricted to a particular chemical class but can be chosen from various chemical types. Preferred compounds are polyphosphoric acid or a polyphosphate such as sodium polyphosphate, a hexametaphosphate such as sodium hexametaphosphate, and thioglycerol.

In a next step a surfactant may be added to the concentrated dispersion. Any of the numerous known surfactants can be used but a preferred product is a commercial saponine.

In order to prepare the dispersion for coating a binder is usually added. Preferred binders are aqueous solutions of polyvinyl alcohol (PVA), polyvinyl pyrrolidone (PVP), polystyrene sulphonic acid (PSSH) and a complex of poly(3,4-ethylenedioxythiophene) and polystyrene sulphonic acid (PEDOT/PSSH). Adding of these binders improves the stability of the nanoparticle dispersions.

When a thus prepared dispersion is coated between two conductive electrodes a so-called Thin Film Inorganic Light Emitting Diode (IILED) is formed. This will now be explained in more detail.

The dispersion is coated on a patterned first conductive electrode. In a preferred embodiment this conductive electrode is an ITO (Indium Tin Oxide) electrode. Thin transparent electrodes of

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evaporated Ag, Au, ... can also be used. The transparent electrode is preferably applied on top of a plastic substrate, e.g. a polyester substrate such as a polyethylene terephthalate substrate, but a glass substrate can also be used. In case the top-electrode (second electrode) is transparent, a non-transparent electrode on glass or plastic can also be used (e.g. Al, Ca, Ag, Mg, Au, etc.) as first electrode. In a preferred alternative embodiment the first conductive electrode is a foil comprising a polythiophene/polyanion conductive complex. Preferably this complex is a poly(3,4-ethylenedioxythiophene)/polystyrene sulphonate complex. A foil comprising such a conductive complex is commercially available as ORGACON, (registered trade name of Agfa-Gevaert N.V.). More details of the incorporation of such a conductive foil can be found in the examples furtheron.

The dispersion to be coated can be applied on top of the first electrode by any suitable coating technique. For the manufacturing of a small prototype spincoating is mostly preferred, but for larger areas doctor blade coating or continuous coating techniques such as used in photographic emulsion coating like air knife coating or curtain coating can be used. The obtained thickness of the dispersion layer is dependent from the nature and concentration of the binder, and from the coating conditions. This thickness is preferably between 50 and 1000 nm.

Finally, a second conductive electrode is applied on top of the coated layer. At least one of the conductive electrodes must be transparent. In a preferred embodiment the second conductive electrode is an aluminum electrode (cathode) applied by vacuum deposition. Also Ca, Mg, LiF/Al, Ag can be used. In case the bottom electrode used is non-transparent (Al, Ag, ...) a transparent electrode should be applied on top of the spincoated ZnS:Cu_xS layer. This can be done by spincoating a PEDOT/PSS dispersion, or by sputtering an ITO layer on top of it, or by evaporation of a thin and transparent conductive metallic layer like Al, Ag, Au, ...

When the resulting device is driven at different direct current bias voltages electroluminescence at a wavelength depending on the nature of the dopant can be observed starting from a certain turn-on voltage. In some cases diode behaviour together with

electroluminescence in both bias directions is observed, as will be shown furtheron by the examples.

The present invention will now be illustrated by the following examples without however being limited thereto.

EXAMPLES

1. Green emitting single layer ILEDs

1.1. Preparation of the Zn(Cu(0.05%))S-dispersion :

The following solutions were prepared :

Solution 1	
Zn(acetate) ₂ .2H ₂ O	131.7 g
Na ₄ EDTA	12 g
Cu(acetate) ₂ .4H ₂ O	54 mg
Water	to 600 ml

Solution 2	
Na ₂ S.9H ₂ O	113.6 g
NH ₃ (26%)	5 ml
Water	to 600 ml

Solution 3	
5-methyl-1,2,4-triazolo-(1,5-a)-pyrimidine-7-ol	40 g
NaCl	58.44 g
Water	to 600 ml

The ZnS:Cu(0.05%) dispersion was prepared as follows:

To solution 3, stirred at 1500 rpm at room temperature solutions 1 and 2, both held at room temperature, were added

simultaneously at a flow rate of 500 ml/min. This is the predispersion A comprising ZnS:Cu - particles.

1.2. Washing of the ZnS:Cu - dispersion:

To 1000 ml of predispersion A, 1000 ml of a 2% polyphosphoric acid solution in water was added and this dispersion was diafiltrated through a Fresenius F60 cartridge. The dispersion was concentrated to 1000 ml and washed at this level by using 5000 ml of a 2% solution of polyphosphoric acid in water.

After the washing, this dispersion was concentrated by means of the diafiltration set-up to a concentration of about 40 g ZnS/l. Subsequently, 1 ml of a 12.5% solution of Saponine Quillaya (Schmittmann) in water/ethanol (80/20) solution of per 20 ml dispersion was added. These is dispersion A.

The dispersion was analysed for its particle size distribution (weight average d_{wa}) with the Disc Centrifuge Photosedimentometer Brookhaven BI-DCP. A weight average particle size diameter of about 75 nm was obtained.

Although particle sizes could be measured with DCP, no clear particles could be visualized by Electron Microscopy (SEM, TEM). The measured particle sizes are probably due (as revealed by EM images) to aggregates of nano-sized particles⁽⁶⁾. This is further confirmed by the fact that ultrasonic treatment before the DCP measurement clearly influences the obtained particle size distribution. The longer the time between the ultrasonic treatment and the DCP-measurement, the larger the obtained values for the weight average particle size. Also the polydispersity increases.

XRD-measurements indicate low crystalline ZnS, however the obtained diffraction signal was used in the Debye-Scherrer equation to calculate the crystalline particle size. Depending on the precipitation conditions, particle sizes between 1.5 and 5 nm were found.

Another indication that the primary particles are indeed much smaller as revealed by DCP-measurements, is the fact that the absorption edge of the ZnS-dispersion and/or layer shifts to shorter wavelengths if compared with bulk ZnS (~ 330 nm). This is a well

known phenomenon in quantum dots⁽⁷⁾. Depending on the precipitation conditions, values of the absorption edge for the ZnS dispersions or layers between 275 and 310 nm were found, indicating, according to the Brus equation⁽¹⁹⁾, particle sizes between 1.5 and 5 nm.

Although that the DCP technique does not give information about particles smaller then 10 - 20 nm in case of real nano-particle dispersions the technique gives important information about the largest aggregates present in the dispersion. By applying layer thicknesses by means of spincoating of about 200 - 400 nm, it is important that the weight average particle size diameter as found by DCP after ultrasound treatment, which is also used before spincoating, stays below 150 nm and more prefarably below 100 nm in order to obtain smooth layers.

1.3. Making of the coating dispersions :

To dispersion A, a binder was added according to table I, in order to stabilize further the dispersion and allow for an homogeneous coating.

Table I:

Coating dispersion	Dispersion A	Binder	Theoretical volume ratio ZnS/Polymer in the layer
A1	16.8 ml	3.2 ml of a 5.8% polystyrene sulfonic acid in water	50/50
A2	19.1 ml	0.9 ml of a 5.8% polystyrene sulfonic acid in water	80/20
A3	16.4 ml	3.6 ml of a 5 % Polyvinylpyrrolidone (LUVISKOL K-90; BASF)	50/50
A4	18.96 ml	1.04 ml of a 5 % Polyvinylpyrrolidone (LUVISKOL K-90; BASF)	80/20

1.4. Preparation of the Thin Film Inorganic Light Emitting
Diodes on ITO:

The device construction is depicted in figure 1. Fig. 1a shows the layer assemblage. ITO (21) on a PET (20) substrate (6 cm x 6 cm x 175 μ m) with a surface conductivity of about 80 Ohm/Sq was patterned by using HNO₃. Two borders of about 1.5 cm were treated with HNO₃ in order to destroy the conductivity. The resulting material comprises a conductive area in the middle of the material with dimensions 6 cm x 3 cm. Subsequently the coating dispersions were spincoated on this substrate. The dry layer (22) thickness varied between 150 and 400 nm depending on the binder and the rotation frequency of the spincoater. A 300 nm thick aluminum electrode (23) (cathode) was vacuum deposited on the spincoated ZnS:Cu/binder layer at 10⁻⁶ Torr through a mask. The emission area was 25 mm². Figures 1b, 1c and 1d separately show the patterning of the different layers, and Fig. 1e shows a top view of the complete patterned ILED.

The device was driven at different direct current bias voltages. Table II lists the turn-on voltages at which green electroluminescence at 515 nm was observed. The electroluminescence started as soon as currents of 5 - 15 mA were attained. These currents correspond to an exponential offset of the I/V-curve (diode behaviour). Life times are listed more quantitatively: A means EL light was only observed for less than 5 seconds, B means it was observed between 5 seconds and 3 minutes and C means that the electroluminescence could be observed for longer than 3 minutes.

Table II: ILEDs on ITO

Sample	Bias	Turn-on Voltage	EL Bright ness	Life Time
A1	+	10 V	+	C

A2	+	8 V	+	B
A3	+	11 V	++	C
A4	+	10 V	+	B

1.5. Preparation of the Thin Film Inorganic Light Emitting Diodes on ORGACON™:

Instead of ITO, the transparent conductive film ORGACON (coated poly(3,4-ethylenedioxythiophene)/polystyrene sulphonic acid complex on a PET substrate), trade mark of Agfa-Gevaert was used for the device construction. The construction is represented in figure 2, which is similar to fig. 1 with ORGACON™ instead of ITO.

An ORGACON foil was cut into 6 cm x 6 cm samples. Subsequently, the resist AZ7217 (Clariant) was spincoated on the samples and baked for 30 minutes at 90°C. The dry layer thickness was about 2-3 µm. This treatment was followed by an UV-exposure through a mask (ca 1 minute at 4mW/cm²), in order to illuminate the middle part (6 cm x 3 cm) of the resist, according to the ITO pattern of figure 1. The sample was then given a prebake for 45 seconds at 110°C and followed by a development step for 40 seconds in the AZ351B developer (Clariant). In order to obtain good adhesion a pre-exposure bake for 30 minutes at 110°C was given. Subsequently, the non protected areas at the two borders were desactivated by dipping the sample in a 1% NaClO solution for 20 seconds. This step was followed by rinsing with water and drying. Then, a full plane exposure for 1 minute at 4 mW/cm² was given and the resist was removed by developing in isopropanol for 90 seconds. Subsequently, the samples were washed with water and dried. The resulting material comprises a conductive area (ca 1500 Ohm/Sq) in the middle of the material with dimensions 6 cm x 3 cm, similar as is depicted in figure 1 for the ITO samples.

Subsequently the coating dispersions were spincoated on this substrate. The dry layer thickness varied between 150 and 400 nm depending on the binder and the rotation frequency of the spincoater. A 300 nm thick aluminum electrode (cathode) was vacuum deposited on the spincoated ZnS:Cu/binder layer at 10^{-6} Torr through a mask. The emission area was 25 mm².

The device was driven at different direct current bias voltages. Table III lists the turn-on voltages at which green electroluminescence at 515 nm was observed. The electroluminescence started as soon as currents of 5 - 15 mA were attained. This currents correspond to an exponential offset of the I/V-curve (diode behaviour). Life times are listed more quantitatively: A means EL light was only observed for less then 5 seconds, B means it was observed between 5 seconds and 3 minutes and C means that the electroluminecence could be observed for longer then 3 minutes.

Table III: ILEDs on ORGACON

Sample	Bias	Turn-on Voltage	EL Bright ness	Life Time
A1 (ORGACON)	+	4 V	+++	C
A2 (ORGACON)	+	4 V	++	B
A3 (ORGACON)	+	4 V	+++	C
A4 (ORGACON)	+	4 V	++	B

2. Blue-green emitting single layer ILEDs

2.1. Preparation of the Zn(Cu(0.05%))S-dispersion :

The following solutions were prepared :

Solution 4	
ZnCl ₂	81.8 g
CuCl	30 mg
Water	to 600 ml

Solution 5	
Na ₂ S.9H ₂ O	113.6 g
NH ₃ (26%)	7.2 ml
Water	to 600 ml

Solution 6	
5-methyl-1,2,4-triazolo-(1,5-a)-pyrimidine-7-ol	40 g
Water	to 1000 ml

The ZnS:Cu(0.05%) dispersion was prepared as follows:

To solution 6, stirred at 1500 rpm at room temperature solutions 4 and 5, both held at room temperature, were added simultaneously at a flow rate of 500 ml/min. This is the predispersion B comprising ZnS:Cu - particles.

2.2. Washing of the ZnS:Cu - dispersion:

To 1000 ml of predisperser B, 1000 ml of a 2% polyphosphoric acid solution in water was added and this dispersion was diafiltrated through a Fresenius F60 cartridge. The dispersion was concentrated to 1000 ml and washed at this level by using 5000 ml of a 2% solution of polyphosphoric acid in water.

After the washing, this dispersion was concentrated by means of the diafiltration set-up to a concentration of about 40 g ZnS/l. Subsequently, 1 ml of a 12.5% solution of Saponine Quillaya (Schmittmann) in water/ethanol (80/20) solution of per 20 ml dispersion was added. These is dispersion B.

The dispersion was analysed for its particle size distribution (weight average d_{wa}) with the Disc Centrifuge Photosedimentometer Brookhaven BI-DCP. A weight average particle size diameter of about 60 nm was obtained.

2.3. Making of the coating dispersions :

To dispersion B, a binder was added according to table IV, in order to stabilize further the dispersion and allow for an homogeneous coating.

Table IV:

Coating dispersion	Dispersion B	Binder	Theoretical volume ratio ZnS/Polymer in the layer
B1	16.8 ml	3.2 ml of a 5.8% polystyrene sulfonic acid in water	50/50
B2	19.1 ml	0.9 ml of a 5.8% polystyrene sulfonic acid in water	80/20
B3	16.4 ml	3.6 ml of a 5 % Polyvinylpyrrolidone (LUVISKOL K-90; BASF)	50/50
B4	18.96 ml	1.04 ml of a 5 % Polyvinylpyrrolidone (LUVISKOL K-90; BASF)	80/20

2.4. Preparation of the Thin Film Inorganic Light Emitting Diodes on ORGACON™:

The patterned ORGACON™ film as described in example 1 (1.5) was used. Subsequently the coating dispersions were spincoated on this substrate. The dry layer thickness varied between 150 and 400 nm depending on the binder and the rotation frequency of the spincoater. A 300 nm thick aluminum electrode (cathode) was vacuum deposited on the spincoated ZnS:Cu/binder layer at 10^{-6} Torr through a mask. The emission area was 25 mm².

The device was driven at different direct current bias voltages. Table V lists the turn-on voltages at which blue-green electroluminescence around 490 nm was observed. The electroluminescence started as soon as currents of 5 - 15 mA were attained. This currents correspond to an exponential offset of the I/V-curve (diode behaviour). Life times are listed more quantitatively: A means EL light was only observed for less then 5 seconds, B means it was observed between 5 seconds and 3 minutes and C means that the electroluminecence could be observed for longer then 3 minutes.

Table V: Blue-green ILEDs on ORGACON

Sample	Bias	Turn-on Voltage	EL Bright ness	Life Time
B1 (ORGACON)	+	4 V	++	B
B2 (ORGACON)	+	4 V	++	A
B3 (ORGACON)	+	4 V	+++	C
B4 (ORGACON)	+	4 V	+++	A

3. Orange-yellow emitting single layer ILEDs

3.1. Preparation of the ZnS:Mn - dispersion :

The following solutions were prepared:

Solution 7	
Zn(acetate) ₂ .2H ₂ O	150.4 g
Mn(acetate) ₂ .2H ₂ O	4.85 g
Water	to 600 ml

Solution 8	
Na ₂ S.9H ₂ O	123.4 g
NaOH (50%)	3.1 ml
Water	to 600 ml

Solution 9	
5-methyl-1,2,4-triazolo-(1,5-a)-pyrimidine-7-ol	60 g
Water	to 800 ml

To solution 9, stirred at 1500 rpm at 80°C, solutions 7 and 8, both held at room temperature, were added simultaneously at a flow rate of 500 ml/min. This results in predispersion C comprising ZnS:Mn - particles.

3.2. Washing of the Zn(Cu)S - dispersion :

To 1000 ml of this predispersion, 1000 ml of a 2% Na-polyphosphate solution in water was added and this dispersion was diafiltrated through a Fresenius F60 cartridge. The dispersion was concentrated to 1000 ml and washed at this level by using 6000 ml of a 2% solution of Na-polyphosphate in water.

After the washing, this dispersion was concentrated by means of a diafiltration set-up to a concentration of about 35 g ZnS/l. Subsequently, 1 ml of a 12.5% solution of Saponine Quillaya (Schmittmann) in water/ethanol (80/20) solution per 20 ml dispersion was added. This is the final ZnS:Mn dispersion C.

The dispersion was analysed for its particle size distribution with the Disc Centrifuge Photosedimentometer Brookhaven BI-DCP. A weight average particle size diameter of about 122 nm was obtained.

3.3. Making of the coating dispersions :

To 16.8 ml dispersion C, 3.2 ml of a 5 % polyvinylpyrrolidone (LUVISKOL K-90; BASF) solution in water was added in order to stabilize further the dispersion and allow for an homogeneous coating.

3.4. Preparation of the Thin Film Inorganic Light Emitting Diodes on ITO:

ITO on a PET substrate (175 µm) with a surface conductivity of about 80 Ohm/Sq was patterned as described in example 1 (1.4). Subsequently the coating dispersion C was spincoated on this substrate. The dry layer thickness varied between 150 and 400 nm

depending on the binder and the rotation frequency of the spincoater. A 300 nm thick aluminum electrode (cathode) was vacuum deposited on the spincoated ZnS:Cu/binder layer at 10^{-6} Torr through a mask. The emission area was 25 mm².

At a forward bias of 7 V orange-yellow (590 nm) electroluminescence could be observed during 60 seconds.

3.5. Preparation of the thin film Inorganic Light Emitting Diodes on ORGACON™

The patterned ORGACON™ film as described in example 1 (1.5) was used. Subsequently the coating dispersions were spincoated on this substrate. The dry layer thickness varied between 150 and 400 nm depending on the binder and the rotation frequency of the spincoater. A 300 nm thick aluminum electrode (cathode) was vacuum deposited on the spincoated ZnS:Cu/binder layer at 10^{-6} Torr through a mask. The emission area was 25 mm².

At a forward bias of 4 V clear orange-yellow (590 nm) electroluminescence could be observed during 30 seconds.

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